Metal salt doped polyaimethylsiloxaneurea copolymers:

Novel materials with unusual properties

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hermoplastic polydimethylsiloxane-urea (TPSU) copolymers were doped with metal salts (CoCl₂.6H₂O, Zn(CH₃COO)₂.2H₂O and ZnCl₂) in solution in different concentrations and homogeneous films were produced after solvent evaporation. Influence of the type of the metal salt and its concentration on the structure, morphology, and properties of TPSU copolymers were investigated. FTIR spectroscopy indicated the interaction of metal salts mainly with the urea hard segments, which was supported by DSC results. Stress-strain tests showed slight improvement in modulus and tensile strength by the incorporation of metal salts. The most unusual observation regarding the metal salt doped TPSUs were their water absorption profiles. TPSU is inherently hydrophobic and absorbs only 0.5% by weight of water at equilibrium at room temperature, On the other hand depending on the structure of the metal salt used and its concentration, water absorption of the TPSU blends increased dramatically from 0.5% to well over 900% by weight. converting completely hydrophobic TPSU into a hydrogel.





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Introduction

Polydimethylsiloxane (PDMS) is an interesting polymer with unusual combination of properties. PDMS has very low glass transition temperature (Tg = -123 °C) resulting in an extremely flexible backbone. PDMS has very high gas permeability, low electrical and thermal conductivity and excellent oxidation and thermal resistance. PDMS has very low Hildebrand solubility parameter $(\delta = 15.3 \text{ MPa}^{1/2})$ and surface tension (20.4 mN/m) which makes it very hydrophobic and water repellant. Due to its very low Tg and extreme backbone flexibility PDMS does not show any mechanical strength at room temperature. Therefore, PDMS polymers are always crosslinked and highly filled with fumed silica for all practical applications (1, 2). Polydimethylsiloxane-urea segmented copolymers are thermoplastic (TPSU) materials with very good thermal and mechanical properties (3,4). Unlike covalently crosslinked PDMS rubbers, TPSU displays a microphase separated morphology, where urea hard segment (HS) domains are distributed in a continuous PDMS soft segment (SS) matrix (3-5). Mechanical strength of TPSU arises from the strong hydrogen bonding (physical crosslinks) present in urea HS. This has been experimentally demonstrated by plotting the ultimate tensile strengths of TPSUs as a function of their hard segment contents, which gave a straight line going through origin (6), clearly showing no significant effect of PDMS soft matrix on the tensile strength of TPSU.

We have been investigating structure-morphology-property behavior of TPSUs and the influence of various parameters, such as PDMS molecular weight, hard segment content and chain extender type on thermal, mechanical, and viscoelastic properties (7-9). We also investigated the influence of fumed silica fillers on tensile properties of TPSU, where we observed that incorporation of silica did not affect the Tg value, did not interfere significantly with the hydrogen bonding between urea groups, but improved the tensile and thermomechanical properties (10).

In this study we investigated the effect of metal salt incorporation on physical and mechanical properties of TPSU. For this purpose, CoCl₂.6H₂O, Zn(CH₃COO)₂.2H₂O and ZnCl₂ were incorporated into TPSU through solution blending. To understand the influence of the amount of metal salt on TPSU properties three different [Metal salt]/[Urea] stoichiometric ratios (0.25, 0.50 and 1.0) were used. Polymeric composites obtained were characterized by spectroscopic techniques, thermal analysis, stress-strain tests, water contact angle and water absorption measurements.

Experimental Materials

Aminopropyl terminated polydimethylsiloxane oligomer (PDMS-NH2) with a molecular weight Mn=3200 g/mol was kindly supplied by Wacker Chemie, Munich, Germany. Bis(4isocyanatocyclohexyl)methane (HMDI) with a purity better than 99.5% was obtained from Bayer, Germany. Reagent grade cobalt(II) chloride hexahydrate (FW=237.90 g/mol), zinc(II) chloride (FW=136.29 g/mol), zinc(II) acetate dihydrate (FW=219.49 g/mol), tetrahydrofuran (THF) and isopropyl alcohol (IPA) were obtained from Riedel de Haen. Metal salts were dried in 50 °C vacuum oven for 24 hours before use to remove adsorbed moisture. Solvents were used as received.

Polymer synthesis

TPSU copolymer was synthesized by the stoichiometric reaction of PDMS-NH2 and HMDI in IPA, at room temperature, in a three-neck, round bottom flask, fitted with a nitrogen inlet, stirrer and an addition funnel. 1.574 g HMDI (6.0 mmole) was introduced into the reactor and dissolved in 15 g of IPA. 19.200 g PDMS-NH2 oligomer (6.0 mmole) was weighed into a flask, dissolved in 30 g of IPA, and introduced into the addition funnel. Polymer was obtained by the dropwise addition of PDMS-NH2 solution onto HMDI solution in the reactor in approximately 15 minutes. Completion of the reaction was determined by FTIR spectroscopy, by the disappearance of strong isocyanate peak at 2270 cm⁻¹. TPSU polymer solution was poured into a Teflon mold and the solvent was evaporated at room temperature overnight and then in a vacuum oven at 50 °C until constant weight. Chemical structure of the TPSU copolymer is shown in Figure 1. Its urea hard segment content is 10.9% by weight or 0.578 mmol/g, its urea equivalent weight is 1731 g/eq.

Preparation of metal salt containing TPSU

TPSU/Metal salt blends with 3 different [Metal salt]/[Urea] concentrations of 0.25, 0.50 and 1.0 were prepared. Calculated amounts of TPSU and metal salts were separately dissolved in the solvent to prepare dilute (ca. 10% by weight) solutions. They were mixed and stirred with a magnetic bar for about 10 minutes. TPSU/metal salt solutions obtained were all clear and homogeneous. Thin films with approximate dimensions of 50x50x1 mm were prepared by casting the blend solutions into Teflon molds and drying. To prevent bubble formation in the films, the solvent was first evaporated at room temperature, then in an air oven at 50 °C and finally in a vacuum oven at 50 °C, until constant weight. Films obtained were kept in sealed plastic bags, in a desiccator.

Characterizations methods

Fourier Transform Infrared (FTIR) spectra were recorded on a Nicolet 6700 spectrophotometer with a resolution of 4 cm⁻¹, using thin films cast on KBr discs from blend solutions. Differential Scanning Calorimetry (DSC) analyses were obtained on a TA Q100 instrument, under nitrogen atmosphere with



Figure 1. Chemical structure of TPSU prepared by stoichiometric reactions.



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a heating rate of 10 K/min. Temperature and enthalpy calibration of DSC was obtained by using indium, lead, and tin standards. Stress-strain tests were carried out on an Instron Model 4411 Universal Tester, at room temperature, with a crosshead speed of 25 mm/min. For stress-strain tests, dog-bone type specimens were punched out of thin copolymer films using a standard die (ASTM D 1708). Static water contact angle measurements were performed at 23±1 °C using 5 µL droplets of deionized, triple distilled water on a Dataphysics OCA 35 goniometer equipped with SCA 20 software. An average of 10 contact angle readings were taken for each sample. Water absorption of the films were determined by immersing them into deionized and triple distilled water at room temperature (23.0±1.0 °C). Percent water absorption was determined gravimetrically by taking the films out of water at desired time intervals, removing the excess water on the film surfaces with a paper towel and weighing them on an analytical balance.

Results and discussion

Metal ion containing polymers display interesting properties depending on the type and nature of the metallic ion, counterion and the concentration of the additive and may find use in electrical, microelectronic, optoelectronic, and medical applications. Polymer properties that can be improved include, higher surface or bulk conductivity. enhanced mechanical strength, improved optoelectronic and other physicochemical properties. Metal containing polymers can be produced by direct polymerization of metal containing monomers or through solution blending, melt compounding, plasma polymerization or mechanochemical synthesis (11-15). In this study effect of CoCl₂.6H₂O, Zn(CH₃COO)₂.2H₂O and ZnCl₂ incorporation on physical and mechanical properties of TPSU was investigated. Three different [Metal salt]/[Urea] stoichiometric ratios (0.25, 0.50 and 1.0) were used. Compositions of the blends prepared and their Tg values are provided in Table 1.

FTIR studies

TPSU copolymers prepared by the stoichiometric reactions of diisocyanates and PDMS oligomers have uniform urea hard segments (HS) and display excellent microphase separation, where highly polar urea HS domains are distributed in continuous PDMS soft segment (SS) matrix (4, 5, 16, 17). Since PDMS matrix is non-polar but the urea HS is very polar, it is expected that metal salts will preferentially interact with the urea HS. Infrared spectroscopy (FTIR) is a simple but powerful technique to investigate the intermolecular interactions in polymer blends due to significant peak shifts observed (18). FTIR spectrum of TPSU is reproduced in Figure 2, where important peak regions are marked as (1) N-H region (3500-3200 cm⁻¹), (2) urea carbonyl region (1700-1500 cm⁻¹) and (3) siloxane (Si-O-Si) region (1300-950 cm⁻¹).

Characteristic absorption bands in the FTIR spectrum of TPSU, given in Figure 2, are: (1) a well-defined urea N-H peak centered at 3335 cm⁻¹, (2) a strongly hydrogen bonded carbonyl peak at 1628 cm⁻¹ (amide I), and another strong peak at 1568 cm⁻¹ due to H-N-C=O stretching (amide II), and (3) a very sharp and symmetrical Si bonded CH_a deformation peak at 1259 cm⁻¹ and a doublet at 1101 and 1082 cm⁻¹ due to asymmetric Si-O-Si stretching. Due to their ionic nature, a strong interaction between the salts incorporated and highly polar urea groups are expected in the TPSU blends prepared. To investigate the nature of interaction FTIR spectroscopy is used. For a better comparison expanded N-H, urea carbonyl (amide I and amide II) and siloxane (Si-O-Si) regions of the FTIR spectra for TPSU and its blend with metal salt are reproduced in Figures 3-5.

It is interesting to note that no change in the peak positions or intensities are observed in the siloxane region in Figures 3-c, 4-c and 5-c, clearly indicating no interaction between the metal salts and the dimethylsiloxane [Si(CH_a)_a-O-Si(CH_a)_a] backbone in TPSU. DSC results provided in Table 1 on the Tg values of TPSU and its blends also strongly support this observation. On the other hand, very slight shifts towards longer wavenumbers are observed in the N-H peaks of all blends (Figures 3-a, 4-a and 5-a). Major peak changes are observed in the 1700-1500 cm⁻¹ urea carbonyl region, for CoCl₂ and ZnCl₂ doped TPSU. As shown in Figure 3-b, very strong amide I and amide II peaks present in TPSU at 1628 and 1568 cm⁻¹ respectively, got much weaker in CoCl_a blends and a new very strong peak at 1600

Table 1. Compositions of TPSU/Metal salt blends

Metal salt	Solvent	[M ²⁺]/[Urea]	Metal Salt (Weight %)	Tg (°C)
TPSU	IPA			-123
CoCl ₂ .6 H ₂ O	THF	1.00	12.1	-123
CoCl ₂ .6 H ₂ O	THF	0.50	6.43	-122
CoCl ₂ .6 H ₂ O	THF	0.25	3.32	-123
ZnCl ₂	IPA	1.00	7.30	-123
ZnCl ₂	IPA	0.50	3.79	-122
ZnCl ₂	IPA	0.25	1.93	-123
Zn(CH ₃ COO) ₂ .2H ₂ O	IPA	1.00	11.3	-121
Zn(CH ₃ COO) ₂ .2H ₂ O	IPA	0.50	5.96	-123
Zn(CH ₃ COO) ₂ .2H ₂ O	IPA	0.25	3.07	-123



Figure 2. FTIR spectrum of TPSU, where critical peak regions are marked. (1) N-H region (3500-3200 cm⁻¹), (2) urea carbonyl region (1700-1500 cm⁻¹) and (3) siloxane (Si-O-Si) region (1300-950 cm⁻¹).

cm⁻¹ was observed. As for ZnCl₂ doped systems, again the amide I and amide II peaks of TPSU got much weaker in the blends and two new and strong peaks centered at 1608 and 1580 cm⁻¹ were observed (Figure 4-b). We believe these results clearly indicate strong intermolecular interaction between the urea groups and CoCl₂ and ZnCl₂. Very interestingly and somewhat unexpectedly no change in the urea peaks centered at 1628 and 1568 cm⁻¹ respectively was observed in TPSU/Zn(CH₃COO)₂ blends (Figure 5-b). This indicates very weak or no interaction between urea groups and the zinc acetate.

Tensile tests

When an inorganic filler is added to a polymeric material, improvements in tensile properties are usually observed. We demonstrated significant improvements in tensile properties of TPSUs by incorporation of hydrophobic fumed silica (10). Stress-strain tests were performed on the metal salt/ TPSU blends to understand the influence of the type and amount of metal salt incorporation on tensile properties. Stress-strain curves obtained are reproduced in Figure 6.





Figure 3. (a) Expanded N-H (3500-3200 cm⁻¹), (b) urea carbonyl (1700-1500 cm⁻¹) and (c) siloxane (1300-950 cm⁻¹) regions of the FTIR spectra for TPSU blends with CoCl₂.



Figure 4. (a) Expanded N-H (3500-3200 cm⁻¹), (b) urea carbonyl (1700-1500 cm⁻¹) and (c) siloxane (1300-950 cm⁻¹) regions of the FTIR spectra for TPSU blends with ZnCl₂.



Figure 5. (a) Expanded N-H (3500-3200 cm⁻¹), (b) urea carbonyl (1700-1500 cm⁻¹) and (c) siloxane (1300-950 cm⁻¹) regions of the FTIR spectra for TPSU blends with Zn(CH₃COO)l₂.



Figure 6. Stress-strain curves for TPSU/metal salt blends.

In CoCl₂ and ZnCl₂ containing blends slight improvements in the Young's modulus and tensile strength values of the materials are observed with an increase in the amount of metal salt. Interestingly, no effect on tensile properties is observed in Zn(CH₃COO₂) containing materials where stress-strain curves obtained were almost identical regardless of the amount of salt incorporation. Stressstrain data obtained are also summarized in Table 2. A slight increase in Young's modulus and the ultimate tensile strength values in CoCl, and ZnCl, containing systems most probably indicate the presence of intermolecular interactions between urea groups and the metal salts. However, since this is

obtained by breaking fairly strong hydrogen bonding within the urea hard segments, the improvement is not significant.

Contact angles and water absorption on TPSU and metal salt blends

PDMS is one of the most hydrophobic polymers with a surface tension or surface energy of about 20 mN/m or 20 mJ/m². Static water contact angle measured on PDMS rubber surface is around 110°. Due to its very low surface energy, when incorporated into copolymers PDMS segments migrate to the air-polymer surface making them hydrophobic. In this study we

prepared a PDMS-urea copolymer (TPSU), which consisted of 90% by weight PDMS. TPSU is a hydrophobic polymer (1, 2, 16, 17) and displays a static water contact angle of 112° as shown in Figure 7-a. To understand the influence of polar metal salt incorporation into on the surface hydrophobicity of TPSU blends we determined the static water contact angles. Images of the initial static water contact angles measured on virgin TPSU and metal salt/TPSU (1/1) blend surfaces are reproduced in Figure 7. Static water contact angles measured on all samples are summarized in Table 3. As can be seen in Figure 7, while virgin TPSU has a static water contact angle of 112°, blends



Table 2. Tensile Properties of TPSU/Metal salt blends

Sample Code	[M ²⁺]/[Urea]	Modulus (MPa)	Tens. Str. (MPa)	Elongation (%)
TPSU		3.90	5.97	580
CoCl ₂ .(1.00)	1.00	9.10	6.70	340
CoCl ₂ .(0.50)	0.50	8.90	6.87	430
CoCl ₂ .(0.25)	0.25	5.80	5.52	450
ZnCl ₂ .(1.00)	1.00	6.60	7.07	430
ZnCl ₂ .(0.50)	0.50	6.50	8.30	480
ZnCl ₂ .(0.25)	0.25	5.10	7.82	570
Zn(CH ₃ COO) ₂ .(1.00)	1.00	4.90	5.97	580
Zn(CH ₃ COO) ₂ .(0.50)	0.50	4.30	5.80	550
Zn(CH ₃ COO) ₂ .(0.25)	0.25	4.00	5.90	560



Figure 7. Images of the static contact water contact angles on (a) TPSU, (b) TPSU/ $CoCl_2$, (c) TPSU/ZnCl₂ and (d) TPSU/Zn(CH₃COO)₂ (All 1/1)

Table 3. Static Water Contact Angles of TPSU/Metal Salt Blend Films

Sample Code	[M ²⁺]/[Urea]	Contact Angle (°)	
TPSU		112.0±0.8	
CoCl ₂ .(1.00)	1.00	93.5±1.3	
CoCl ₂ .(0.50)	0.50	95.8±1.0	
CoCl ₂ .(0.25)	0.25	98.8±1.5	
ZnCl ₂ .(1.00)	1.00	104.7±1.4	
ZnCl ₂ .(0.50)	0.50	96.3±1.2	
ZnCl ₂ .(0.25)	0.25	99.0±1.4	
Zn(CH ₃ COO) ₂ .(1.00)	1.00	98.0±1.4	
Zn(CH ₃ COO) ₂ .(0.50)	0.50	102.9±1.2	
Zn(CH ₃ COO) ₂ .(0.25)	0.25	104.0±1.4	



Figure 8. Time dependent change in the static water contact angle on TPSU/CoCl_2 (1/1) film. Top numbers indicate time in minutes, bottom numbers show water contact angles in degrees.

containing $CoCl_2$ (Fig. 7-b), $ZnCl_2$ (Fig. 7-c), and $Zn(CH_3COO)_2$ (Fig. 7-d) display 93.5°, 104.7° and 98.0° respectively, indicating a significant reduction in the hydrophobicity of the blend surfaces, which is expected. As shown in Table 3 similar results are observed in all blend surfaces, where a reduction in water contact angle is observed in all samples as a function of their metal salt content.

After measuring the static water contact angles on TPSU and the blend surfaces,

we wanted to keep the water droplet on the surface and observe if there would be any change in the contact angle over time. As well-known, thermodynamic requirement is the formation of lowest energy surfaces. Polymer surfaces are dynamic and depending on the nature of the polymer/substrate interface, they rearrange to minimize the surface energy (19, 20). Therefore, when in contact with air, non-polar groups/segments in a polymer (in case of TPSU the PDMS groups) migrate to the air/polymer interface and when in contact with water, polar groups/segments (in case of TPSU blends, metal salt containing urea domains) move to the polymer/water interface to minimize the surface energy. Images of the time dependent water contact angles on TPSU/ CoCl₂ (1/1) blends are provided in Figure 8, where a substantial decrease in water contact angle is observed with time from 97° (indicating a hydrophobic surface) to 40° (indicating a very hydrophilic surface) in 21 minutes. Change in water contact angle as a function of time for TPSU/CoCl_o (1/1) blends is also plotted in Figure 9. These results clearly indicate major surface rearrangements taking place in TPSU/metal salt blends, as discussed.

When we observed such a dramatic drop in water contact angles of TPSU/CoCl₂ (1/1) blends from 97° to 40° within 20 minutes, we decided to determine the extent of water absorption in these blends. Inherently hydrophobic TPSU absorbs only 0.5% by weight of water at equilibrium at room temperature as shown in Figure 10. Very surprisingly we observed extremely high water absorption levels in metal salt doped TPSU blends as shown in Figures 10, 11 and 12. Amount of water absorption was a strong function of the type of the metal salt and its amount in the blend.

As provided in Figure 10, Zn(CH₂COO) which showed almost no interaction with the urea hard segments in FTIR studies also displays the lowest amount of water absorption when compared with the other blends. TPSU/Zn(CH₂COO)₂ 0.25 blend shows about 8.4% by weight water absorption at equilibrium, while 0.50 blend shows 25% by weight. When compared to virgin TPSU, Zn(CH₃COO)₂ blends show significant increase in water absorption. However, when compared with other blends they are extremely low. Water absorption for TPSU/ ZnCl_a blends are 175% for 0.25, 370% for 0.50 and 380% for 1.0 blend (Figure 11). These are more than an order of magnitude higher when compared with TPSU/ Zn(CH₂COO)₂ blends. Since both cations are zinc(II), these results clearly indicate the strong influence of the anion type on water absorption. CoCl, doped TPSU blends show





Figure 9. Change in static water contact angle as a function of time for $CoCl_2$ (1/1) blend films.



Figure 10. Time dependent water absorption profiles of TPSU/ $Zn(CH_3COO)_2$ blend films at room temperature. (**A**) TPSU, Metal salt/urea ratios: (•) 0.5, and (**B**) 0.25.



Figure 11. Time dependent water absorption profiles of TPSU/ZnCl₂ blend films at room temperature. Metal salt/ urea ratios: (•) 1.0, (\blacksquare) 0.5, and (\blacktriangle) 0.25.



Figure 12. Time dependent water absorption profiles of TPSU/CoCl₂ blend films at room temperature. Metal salt/ urea ratios: (•) 1.0, (\blacksquare) 0.5, and (\bigstar) 0.25.

even higher water absorption levels at equilibrium, reaching well over 900% for (1/1) blend as shown in Figure 12. These results also indicate strong influence of cation type on water absorption in TPSU blends. For a direct comparison we plotted all water absorption results obtained, except TPSU/ Zn(CH_COO), (1/1), in Figure 13, where dramatic influence of the metal salt structure and amount on the extent of water absorption can clearly be seen. We believe the most striking and important result of the water absorption study is the conversion of inherently hydrophobic TPSU to a highly hydrophilic hydrogel through small amounts of metal salt incorporation!



Figure 13. Influence of metal salt structure and amount on the extent of water absorption in TPSU blends. (\blacksquare) Zn(CH₃COO)₂, (\blacksquare) ZnCl₂, and (\blacksquare) CoCl₂.

Conclusions

Effect of metal salt incorporation on physical and mechanical properties of a thermoplastic silicone-urea copolymer (TPSU) was investigated. Three different metal salts, CoCl₂.6H₂O, Zn(CH₂COO)₂.2H₂O and ZnCl₂ were incorporated into TPSU through solution blending at [Metal salt]/[Urea] stoichiometric ratios of 0.25, 0.50 and 1.0, Polymeric composites obtained were characterized by FTIR spectroscopy, DSC analysis, stressstrain tests, static water contact angle and water absorption measurements. FTIR studies showed strong intermolecular interaction between metal salts and the urea hard segments in CoCl, and ZnCl,, but not in Zn(CH₂COO)₂, indicating a strong influence of the anion on blend morphology. Strong interaction between TPSU and CoCl, and ZnCl_a led to an increase in tensile properties. However, the most striking observation was in the water absorption levels of the TPSU blends with CoCl₂ and ZnCl₂, which converted inherently hydrophobic TPSU, which absorbed only 0.5% of water, to a hydrogel, which absorbed well over 900% water by weight. We are currently investigating the conductance of these materials since they may be used as polymer electrolytes.

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